

Synchrotron X-ray structure refinement of Zn_4Sb_3

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Abstract

The structure of the thermoelectric Zn_4Sb_3 is refined using synchrotron X-ray powder diffraction data collected at wavelengths both near to and relatively far from the Zn adsorption edge. In agreement with earlier studies, the compound crystallized in a trigonal structure, space group $R\bar{3}c$ with $a = 12.2406(3)\text{\AA}$, $c = 12.4361(3)\text{\AA}$ at room temperature, and there are three primary sites in the asymmetric unit. Each site contains only one atomic species, in contrast to many previous studies. The primary Zn (36f) site is slightly less than fully occupied, whereas the two Sb sites (18e and 12c) are fully occupied. In addition, several Zn interstitial sites (36f) with low occupancies ($>5\%$) are also present. The results are in agreement with the model proposed by Snyder [1], as opposed to that originally proposed by Mayer [2] and more recently by Mozharivskyj [3]. The refined site occupancies yield an overall stoichiometry which is consistent with that measured experimentally. The presence of interstitial Zn can be understood in terms of charge balance requirements and is likely responsible for the exceptionally low thermal conductivity of this material.

Keywords

Zinc antimonide, Zn_4Sb_3 , crystal structure, structural disorder, Rietveld refinement, Zintl phase.

Introduction

The development of efficient thermoelectric devices for both space and terrestrial applications requires the discovery of materials with a high thermoelectric figure of merit, zT , defined as $\alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ the electrical conductivity and κ the thermal conductivity. Of known thermoelectrics, the compound Zn_4Sb_3 has attracted recent attention because it has the highest reported value of zT at moderate temperatures (reaching almost 1.3 at 400°C) [4,1]. This behavior is a result of the particularly low thermal conductivity of Zn_4Sb_3 , being lower by as much as a factor of five than that of related materials such as ZnSb , $\text{CeFe}_4\text{Sb}_{12}$ and PbTe [1]. In a recent study, this low thermal conductivity was attributed to the presence of stoichiometrically and structurally required interstitial zinc atoms. That is, the chemical bonding scheme of Zn_4Sb_3 , in which two-fifths of the Sb atoms form dimers and thus have charge 2- and the remaining are present as isolated 3- ions, requires an overall Zn:Sb ratio of 13:10 ($\text{Zn}_{3.9}\text{Sb}_3$). Full occupancy, however, by the atomic species on the one Zn site (36f) and two Sb sites (18e and 12c) within the hexagonal structure ($R\bar{3}c$) of Zn_4Sb_3 results in an Zn:Sb ratio of only 6:5. Thus, the presence of interstitial Zn sites with low occupancy yields a composition that obeys the rules of valence. At the same time, such an

interpretation of the crystal chemistry of Zn_4Sb_3 is consistent with the experimentally measured density and fixed stoichiometry of $\text{Zn}_{3.95(5)}\text{Sb}_3$, and the mechanically brittle properties. This structural model can be contrasted against the earliest structure reports of Zn_4Sb_3 in which some occupation of Zn on one of the Sb sites was proposed in order to account for the experimentally measured composition [5], and a very recent report in which the empirical composition is disregarded [3]. Recent studies of synchrotron X-ray powder diffraction data have used either the mixed Zn/Sb site [6] of Mayer or a constrained interstitial model [7].

In this study we have reexamined the structure of ' Zn_4Sb_3 ' in an attempt to resolve the continuing controversy regarding its crystal-chemical nature. By making use of anomalous scattering of Zn at two wavelengths ($f' = -5.7$ and -1.3 for the two data sets) we can distinguish mixed occupancy from vacancies.

Experimental procedure

The powder sample was obtained by direct reaction of the constituent elements from the melt. For this zinc (99.9999%) and antimony (99.999%) shots were combined in a 57.5:42.5 atomic ratio and processed in a silica ampoule.

High-resolution X-ray powder diffraction data were recorded at room temperature in θ - 2θ reflection geometry at NSLS beamline X3B1. The sample was side-drifted onto a quartz zero-background holder, rocked 10° at each point in order to improve sampling statistics. In two separate data collections, X-rays of wavelength 1.14985 and 1.28788 \AA were selected by a double-crystal Si(111) monochromator. High resolution was achieved by analyzing the diffracted beam with a Ge(111) crystal placed before the NaI scintillation counter. Data were collected from 16.000° to 77.765° 2θ and 18.000° to 89.990° 2θ , respectively, for the two wavelengths using a step size of 0.005° and counting time of 5 sec.. The incoming beam was monitored by an ion chamber and the recorded data normalized for its fluctuations and decay

Rietveld refinement was performed simultaneously for the two datasets using the program GSAS [8] with EXPGUI interface [9]. The presence of elemental Zn was detected in the diffraction data and this second phase was included in the model refinement. In addition, a peak of unknown origin at $d = 1.805 \text{ \AA}$ was observed in both histograms and thus the region about this peak was omitted from the analysis.

Refinement Procedure and Results

The initial parameters for the refinement of the structure of Zn_4Sb_3 were taken from Mayer [2], which contains at its core one Zn 36f site and two Sb sites: Sb(1) on an 18e site and Sb(2) on a 12c site, Table 1. The key question to be addressed was the atomic occupancy factors, in particular the possible incorporation of Zn on the Sb(1) site and the existence of additional 36f sites for Zn. Accordingly, the lattice constants, atomic coordinates of the three primary sites, and all profile parameters were refined early in the analysis and fixed at their optimal values for subsequent comparisons of structural models that differed primarily in terms of site occupancies.

Table 1. Structure of Zn_4Sb_3 as originally reported by Mayer [2] and used as the starting point for the present refinements.

Cell: $R\bar{3}c$	a :	12.233 Å	c :	12.428 Å
Atom	Site	x	y	z
Zn(1)	36(f)	0.0794	0.2437	0.4037
Sb(1) [+Zn]	18(e)	0.3554	0	$\frac{1}{4}$
Sb(2)	12(c)	0	0	0.1365

Refinement of the Sb occupancies showed these sites to be fully occupied with occupancy factors typically settling at values just above 1, without improvement in the refinement statistics. Because Zn is a lighter element than Sb, its presence on the Sb(1) site would result in an apparent reduction in the occupancy on this site. Thus, we can immediately conclude that the model proposed by Mayer [2], with partial (11%) Zn occupancy on the Sb(1) site does not describe the true structure of Zn_4Sb_3 .

With the occupancies of the Sb atoms fixed at one and their isotropic thermal displacement parameters optimized and then fixed, the Zn occupancy factor was probed. Because of the high correlation between occupancy factor and thermal displacement parameter, these terms were adjusted cautiously. In all cases, the occupancy factor dropped substantially below 1 (to 0.915) and resulted in a slight but statistically significant improvement in the refinement. As would be expected, the isotropic thermal displacement parameter for this atom also decreased substantially from a highly unreasonable value to one that was about a factor of three greater than that of the Sb atoms.

In the final step, Zn interstitial atoms were introduced at sites determined from our previous single crystal diffraction study, reported in Snyder et al. [1]. Doing so improved the refinement statistics considerably, and the three sites displayed statistically significant occupancy factors. Again, because of the high correlation between occupancy and thermal displacement parameters, these terms were varied cautiously and in the final cycles of the refinement the three interstitial atoms were assigned a fixed isotropic displacement parameter that corresponded to the average value that was

obtained upon varying the three terms independently. The excellent fit to the experimental diffraction data obtained from this model supports the proposal that Zn exists at interstitial positions within the 'core' structure of Zn_4Sb_3 .

Table 2. Comparison of refinement statistics for the models of ' Zn_4Sb_3 ' and the stoichiometries implied. The full occupancy model is as proposed by Mayer [2]; the vacancy model [3] assumes the Zn site to be 91.5% occupied; and the three interstitial model assumes, in addition, vacancies on the primary Zn site, that three Zn interstitial sites exhibit 3.6-6.5% occupancy, Table 3.

Model	R_F (%)	χ^2	x in Zn_xSb_3
Full occupancy	12.31	5.218	3.60
Zn vacancy	12.22	5.136	3.30
Three interstitial	11.62	4.648	3.88

Table 3. Final refinement statistics and crystallographic data for the three interstitial site model of Zn_4Sb_3 .

Space Group	$R\bar{3}c$ (no. 62)
a (Å)	12.2406(3)
c (Å)	12.4361(3)
Z	10
V (Å ³)	1613.693(4)
$R_p \times 100$	3.14
$R_{wp} \times 100$	11.62
$R_F^2 \times 100$ [Hist1]	16.57
$R_F^2 \times 100$ [Hist2]	11.78
χ^2	4.648
Zn(1) x	0.07909(9)
Zn(1) y	0.24318(9)
Zn(1) z	0.40152(9)
Zn(1) Uiso	0.0180(4)
Zn(1) occupancy	0.9153(17)
Sb(1) ¹ x	0.35645(4)
Sb(1) Uiso	0.00751(14)
Sb(2) ¹ z	0.13656(5)
Sb(2) Uiso	0.00733(18)
Zn(2) ² occupancy	0.0607(19)
Zn(3) ² occupancy	0.0364(21)
Zn(4) ² occupancy	0.0649(21)

¹ with remaining coordinates as given in Table 1.

² with fixed isotropic displacement parameter of 0.085 and fixed atomic coordinates as given in [1]: Zn(2) at 0.1574, 0.4207, 0.0715; Zn(3) at 0.242, 0.460, 0.200; Zn(4) at 0.126, 0.2367, 0.276.

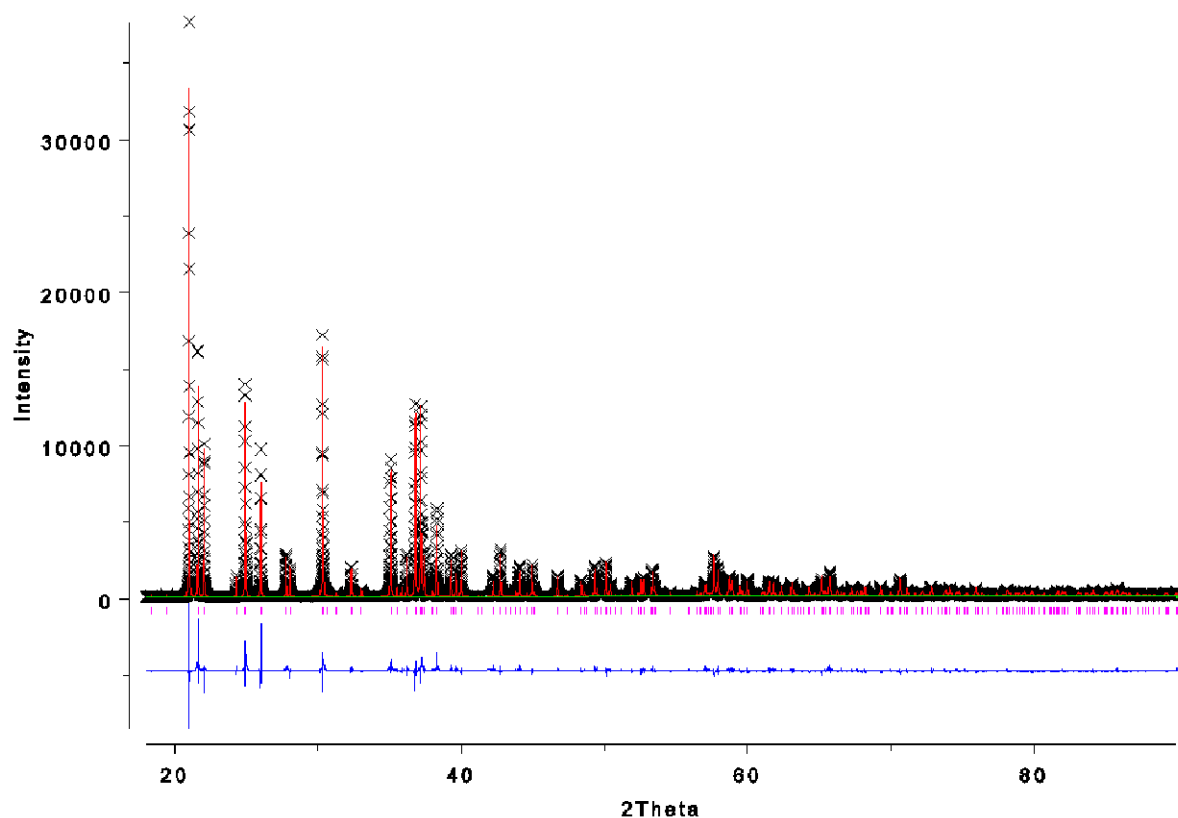
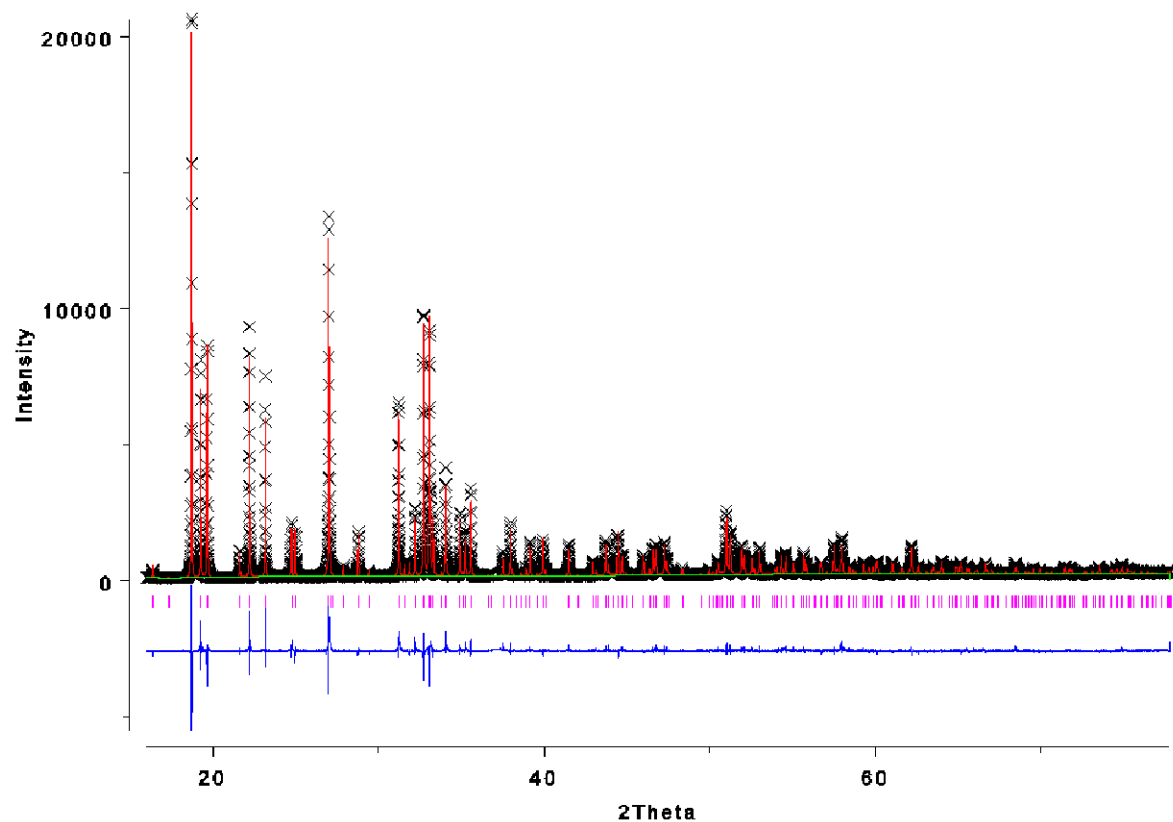


Figure 1. Measured (black) and calculated (red) X-ray diffraction data for the three interstitial site model of Zn_4Sb_3 , Table 3; (a) $\lambda = 1.14985 \text{ \AA}$ and (b) $\lambda = 1.28788 \text{ \AA}$. Difference curve shown in blue and phase peak positions in magenta.

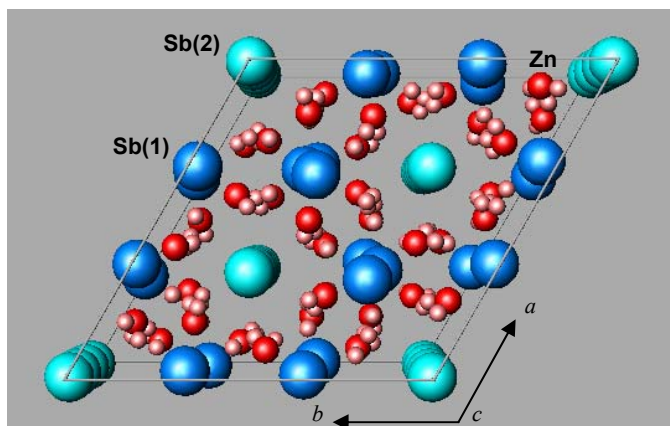


Figure 2. The structure of Zn_4Sb_3 . Primary Zn sites shown as larger red spheres and interstitial sites as smaller pink spheres.

A direct comparison of the refinement statistics of three models of Zn_4Sb_3 are provided in Table 2. The full occupancy model corresponds to that in which the three primary sites are fully occupied and mixed occupancies are not permitted. The vacancy model corresponds to that proposed by Mozharivskij [3] in which the two Sb sites are fully occupied by Sb only, but the Zn site occupancy takes on the refined value of 0.915. The three interstitial model corresponds to that in which the occupancy on the primary site remains below 1 and in addition interstitial Zn atoms are placed at the sites first reported by Snyder [1], without optimization of the atom coordinates. It is immediately apparent that not only does the interstitial model best fit the data, but it also best matches the experimentally determined composition, and density [1]. From this we conclude that the model proposed by Mozharivskij *et al* [3] also fails to correctly describe the structure of Zn_4Sb_3 .

The full crystallographic results obtained from the refinement of the structure assuming the interstitial model is presented in Table 3, and plots comparing the measured and calculated diffraction patterns in Figure 1. Overall, while the integrated peak intensities are well-matched, it is apparent that the shape of the peaks is not entirely accounted for and this is responsible for the relatively high values of R_F and χ^2 values. Finally, we note the refined metallic Zn content was 1.5 wt%

The existence of ‘stoichiometrically required’ interstitial sites is a highly unusual crystallographic feature of Zn_4Sb_3 , but one that is extremely advantageous in terms of thermoelectric properties. The Zn interstitial species are taken to be responsible for the exceptionally low thermal conductivity observed in this material. The presence of Zn vacancies on the primary Zn site, which, in principle, are not stoichiometrically required, surely results from the close proximity of the interstitial sites to the primary site, Figure 2. Located at distances of only 0.96 to 1.68 Å away from the primary sites, it is unlikely that both the primary site and any one interstitial site are simultaneously occupied. Instead, pairs of interstitial sites (with Zn-Zn distances of 2.55 to 2.73 Å) may be simultaneously occupied and replace a single Zn atom that would otherwise reside on the primary site. The Zn

vacancies result in additional structural disorder that presumably also contributes to the low thermal conductivity.

Conclusions

The synchrotron powder X-ray structure refinement performed here strongly supports a model of Zn_4Sb_3 in which stoichiometrically required Zn interstitials are present within the structure. In addition, structural vacancies on the primary Zn site are also present. The results are in agreement with the model proposed by the present authors [1], and in sharp disagreement with the traditional mixed Zn/Sb model of Mayer [2] and a more recent, ‘interstitial-free’ model reported by Mozharivskij [3].

Acknowledgments

This work was funded by the NSF through Caltech’s Center for the Science and Engineering of Materials (MRSEC program). NSLS beamline X3 was partially supported by the Department of Energy under grant no. DE-FG02-86ER 45231. The National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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